Green Synthesis of Pyrazol-chromeno[2,3-*d*]pyrimidinones Using SBA-Pr-SO_3H as an Efficient Nanocatalyst

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ABSTRACT: *Hexagonal mesoporous silica (SBA-15) was prepared and then functionalized by (3-mercaptopropyl)trimethoxysilane. The obtained 3-mercaptopropyl functionalized SBA-15 (SBA-Pr-SH) was then oxidized using H_2O_2 in methanol under an acidic condition to give sulfonic acid functionalized mesoporous silica (SBA-Pr-SO_3H). The latter was characterized using different techniques (including TGA, BET, BJH, CHN, SEM, and TEM) and then used as a catalyst in organic synthesis. In the next step, SBA-Pr-SO_3H catalyzed the three-component reaction of pyrazolone, salicylaldehydes, and barbituric acid in water under reflux condition. Through this procedure various pyrazolchromeno[2,3-d]pyrimidinone derivatives were obtained. The reaction conditions were completely green due to the use of water as a solvent and the presence of an environmentally benign catalyst.*

KEYWORDS: *Multicomponent reactions; Salicylaldehyde; Pyrazolone; Barbituric acid; SBA-Pr-SO_3H, Green synthesis.*

INTRODUCTION

MultiComponent Reactions (MCRs) have been known for above 150 years. The benefits of MCRs are productivity, simple procedure, time-saving manner, and facile execution [1]. Nowadays, MCRs are widely used for the synthesis of heterocyclic compounds. One of the famous N-contain heterocyclic compounds are pyrazole derivatives [2] which recently attracted the attention of chemists and biochemists owing to their wide applications in chemistry, biology, and material science as well [3]. Some pyrazoles with medicinal significance are considered as an analgesic and antipyretic [4], anticonvulsant [5], antidiabetic [6] and antimicrobial agents [7].

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The use of heterogeneous catalysts has attracted the attention of many chemists. SBA family is one of the most applicable substrates which its members are widely used for catalyst preparation due to their highly arranged structure and very high surface area with pore sizes in nanometer ranges [8]. The preparation of MCM-41 by Mobil Corporation scientists in 1992 [9] and then SBA-15 by *Zhao et al*. in 1994 [10, 11] were the main sources of further studies for developing such compounds and their applications. SBA-15 is a mesoporous silica which has a hexagonal structure, controllable pore size, high surface area and high thermal durability. Among the mesoporous silica materials, SBA-15 has the more diffusion free due to the thickness of its pore walls, modifiable surface and appropriate pore size [12]. So far, the internal surface of SBA-15 was modified with different organic compounds which then used as the catalysts [13], sensors [14] and adsorbents [15, 16].

Sulfonic acid modified SBA-15 (SBA-Pr-SO_3H) is a solid acid nanoreactor which is synthesized by treating the free silanol groups on the SBA-15 surface with 3-mercaptopropyl trimethoxysilane to procure SBA-Pr-SH; following oxidation of the thiol group using H_2O_2 [17]. In continuation of our previous works [18-27], we decided to apply this catalyst in the Knoevenagel-Michael addition for the synthesis of pyrazole-based compounds possessing the biological properties.

EXPERIMENTAL SECTION

Melting points were measured using the capillary tube method with an electrothermal 9200 apparatus. FT-IR spectra were recorded from KBr disk using a FT-IR Bruker Tensor 27 instrument. The ^{1}H and ^{13}C NMR was run on a 250 and 62.5 MHz Bruker, respectively. SEM image was obtained on a Philips XL-30 field-emission scanning electron microscope operated at 16 kV, while TEM was carried out on a Tecanai G^2 F30 at 300 Kv.

Synthesis and functionalization of SBA-15

The mesoporous SBA-15 was prepared and functionalized according to our previous report [28, 29] and then, the obtained SBA-Pr-SO_3H was used as a heterogeneous acid catalyst in the following reaction.

Synthesis of pyrazolone 3a-d

Pyrazolone derivatives were prepared from the reaction of hydrazine derivatives and alkyl or aryl acetoacetate in suitable solvents and under conditions mentioned in Table 1. The obtained pyrazolone was recrystallized in EtOH.

General procedure for the synthesis of pyrazol‑chromeno [2,3‑d]pyrimidinones (6a-i)

A mixture of salicylaldehyde derivative (1 mmol), barbituric acid or *N*,*N*-dimethylbarbituric acid (1 mmol) and SBA-Pr-SO_3H (0.02 g) in water (5 mL) was stirred and heated under reflux condition. After 5 min, pyrazolone derivative (1 mmol) was added to it and heated for about 5 h under reflux condition. After completion of the reaction, as indicated by TLC, water was evaporated and the mixture was dissolved in hot EtOH. The catalyst was insoluble and easily removed by filtration. The pure products (**6a-i**) were obtained after cooling of the filtrates. The spectral data for the new compounds are given below.

Spectroscopic data for new compounds(6d-4i)

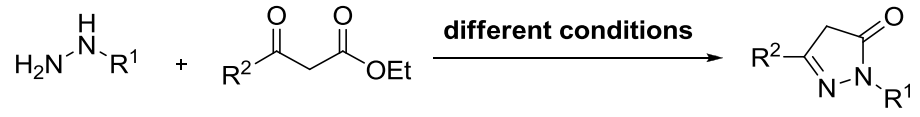
5-(5-hydroxy-3-methyl-1-(4-nitrophenyl)-1H-pyrazol-4-yl)-1,5-dihydro-2H-chromeno[2,3-d]pyrimidine-2,4(3H)-dione (6d)

Yellow powder (yield 98 %); mp: 230-232 °C. FT-IR (KBr), ν_{max} (cm^{-1}): 3617 (OH), 3389 (NH), 33092 (Ar-H), 1688 (C=O), 1643, 1517, 1088. ^{1}H NMR (250 MHz, DMSO-d_6), δ_H (ppm): 2.35 (3H, s, CH_3), 4.37 (s, 2H, NH), 4.79 (1H, s, CH), 7.03-7.22 (m, 4H, Ar-H), 7.93 (d, 2H, *J* = 7, Ar-H), 8.21 (d, 2H, *J* = 9, Ar-H), 10.98 (2H, s, NH), 11.85 (1H, s, OH). ^{13}C NMR (62.9MHz, DMSO-d_6), δ_C (ppm): 11.70 (CH_3), 26.60 (CH), 86.20 (C=C– OH), 116.19 (C=C–O), 117.74, 123.32, 125.33, 125.63, 128.52, 130.10, 143.06, 149.47, 150.06, 154.84, 163.87.

5-(5-hydroxy-3-methyl-1H-pyrazol-4-yl)-1,5-dihydro-2H-chromeno[2,3-d]pyrimidine-2,4(3H)-dione (6e):

White powder (yield 97 %); mp: 250-252 °C. FT-IR (KBr) (ν_{max}/cm^{-1}): 3630 (OH), 3349 (NH), 1735 (C=O), 1644, 1589, 1466, 1033. ^{1}H NMR (250 MHz, DMSO-d_6), δ_H (ppm): 2.47 (3H, s, CH_3), 4.72 (1H, s, CH), 6.46-7.28 (H-Ar), 11.29 (3H, s, NH), 11.18(1H, s, OH). 13C NMR (62.9MHz, DMSO-d_6), δ_C (ppm): 11.59, 26.23, 87.72, 104.81, 118.55, 124.94, 126.94, 128.06, 132.12, 136.65, 143.71, 150.12, 155.84, 160.83, 163.87.

Table 1: Synthesis of pyrazolone derivatives 3a-d.



1 **2** **3a-d**

Entry	No.	R^1	R^2	Conditions/Solvents	Time (min)	Yield (%)	m.p. (°C)	m.p. Lit. (°C)
1	3a	Ph	Me	100 °C/Solvent free	60	>95	127-129	120-127[30]
2	3b	H	Ph	r.t./EtOH	5	90	238-240	235-237[31]
3	3c	H	Me	r.t./EtOH	5	90	220-222	217-219[32]
4	3d	4-$NO_2C_6H_4$	Me	Reflux/HOAc glacial	60	>95	225-227	204-207[30]

5-(5-hydroxy-3-methyl-1H-pyrazol-4-yl) -1,3- dimethyl-1,5-dihydro-2H-chromeno [2,3-d] pyrimidine-2,4(3H)-dione (6f)

White powder (yield 85 %); mp: 234-236 °C. FT-IR (KBr) (ν_{max}/cm^{-1}): 3640(OH), 3369(NH), 1704 (C=O), 1664, 1524, 1481, 1228. MS, *m*/*z*: 340(M^+), 304, 264, 244, 230, 215, 186, 159, 139, 118, 89, 76, 63, 50. ^{1}H NMR (250 MHz, DMSO-d_6), δ_H (ppm): 2.05 (3H, s, CH_3), 3.78(6H, s, CH_3), 4.79 (1H, s, CH), 7.12-7.53 (H-Ar), 11.08(1H, s, NH), 9.30(1H, s, OH). 13C NMR (62.9MHz, DMSO-d_6), δ_C (ppm): 10.32, 27.08, 28.06, 29.27, 40.27, 40.94, 88.22, 105.75, 116.15, 124.72, 125.83, 128.01, 130.08, 149.17, 150.63, 153.02, 161.69.

5-(5-hydroxy-3-methyl-1H-pyrazol-4-yl) -7-nitro -1,5-dihydro-2H-chromeno[2,3-d]pyrimidine -2,4(3H)-dione (6g)

White powder (yield 82 %); mp: 243-245 °C. FT-IR (KBr) (ν_{max}/cm^{-1}): 3620 (OH), 3460 (NH), 1680 (C=O), 1617, 1525, 1184, 1084. ^{1}H NMR (250 MHz, DMSO-d_6), δ_H (ppm): 1.92 (3H, s, CH_3), 5.56 (1H, s, CH), 6.81-8.21 (H-Ar), 10.23 (3H, s, NH), 10.02 (1H, s, OH). ^{13}C NMR (62.5 MHz, DMSO-d_6), δ_C (ppm): 10.37, 18.92, 26.96, 56.45, 90.06, 105.14, 115.47, 124.05, 125.42, 126.79, 130.37, 139.50, 144.26, 151.04, 160.66, 161.97.

5-(5-hydroxy-3-methyl-1H-pyrazol-4-yl)-1,3-dimethyl-7-nitro-1,5- dihydro -2H- chromeno [2,3-d] pyrimidine-2,4(3H)-dione (6h):

White powder (yield 95 %); mp: 237-239 °C. FT-IR (KBr) (ν_{max}/cm^{-1}): 3250 (OH), 3108 (NH), 1617 (C=O), 1574, 1338, 1278, 1084. ^{1}H NMR (250 MHz, DMSO-d_6), δ_H (ppm): 1.95 (3H, s, CH_3), 3.08 (6H, s, CH_3), 5.56 (1H, s, CH), 6.82-8.16 (H-Ar), 11.50 (1H, s, OH), 13.78 (1H, s, NH). ^{13}C NMR (62.5 MHz, DMSO-d_6), δ_C (ppm): 10.73, 18.92, 26.96, 56.45, 90.06, 105.14, 115.47, 124.05, 125.42, 126.79, 130.37, 139.50, 144.26, 151.04, 160.66, 161.97, 165.50.

5-(5-hydroxy-3-phenyl-1H-pyrazol-4-yl)-1,3-dimethyl-7-nitro-1,5-dihydro -2H- chromeno[2,3-d]pyrimidine-2,4(3H) -dione (6i)

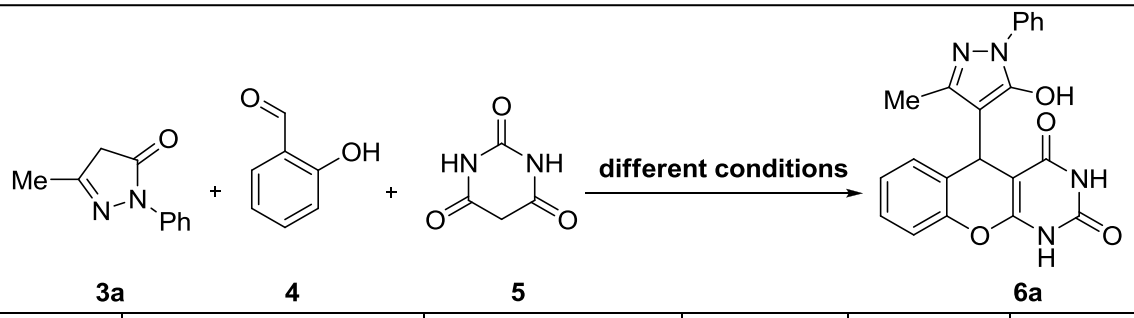
White powder (yield 90%); mp: 218-220 °C. FT-IR (KBr) (ν_{max}/cm^{-1}): 3368 (OH), 3211(NH), 1711 (C=O), 1522, 1338, 1206, 1036. ^{1}H NMR (250 MHz, DMSO-d_6): δ_H (ppm): 3.02 (6H, bs, CH_3), 5.10 (1H, s, CH), 6.85-8.13 (H-Ar), 11.42(1H, s, OH), 13.78 (1H, s, NH). ^{13}C NMR (62.5 MHz, DMSO-d_6), δ_C (ppm): 18.94, 28.31, 115.34, 124.34, 128.55, 129.16, 132.38, 139.69, 152.11, 160.53, 161.39.

RESULT AND DISCUSSION

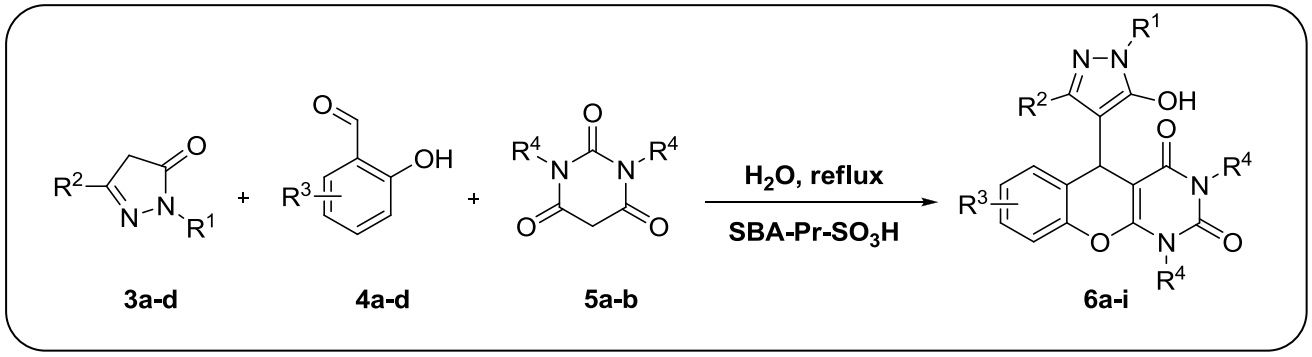
Synthesis of pyrazol-chromeno[2,3-d]pyrimidinones

In this study, the role of pyrazolone was studied in the synthesis of pyrazol-chromeno[2,3-*d*]pyrimidinones. For this aim, derivatives of pyrazolone **3a-d** were prepared through the reaction of corresponding hydrazine **1** and alkyl acetoacetate **2** under different conditions as shown in Table 1. The obtained pyrazolone **3a-d** was then applied in the three component reaction with salicylaldehyde **4** and barbituric acid derivative **5**. In order to determine the optimized conditions for this reaction, preparation of **6a** was studied under different reaction conditions as shown by the results in Table 2. Among the tested conditions, the best results were obtained in water under refluxing after 5 h using SBA-Pr-SO_3H. Additionally, it was found that the catalyst has the significant role in this reaction since in the absence of the catalyst, the reaction yield was very low even after 10 hours.

Table 2: Optimization of the reaction conditions for the synthesis of 6a.



Entry	Catalysts	Solvents	Conditions	Time (h)	Yields (%)
1	_	H_2O	reflux	10	20
2	SBA-Pr-SO_3H	H_2O	reflux	5	>95
3	SBA-Pr-SO_3H	EtOH	reflux	7	50
4	SBA-Pr-SO_3H	_	120 °C	10	<5
5	SBA-Pr-SO_3H	EtOH/ H_2O(1:1)	reflux	6	70
6	SBA-Pr-SO_3H	EtOH/ H_2O(1:4)	reflux	6	80



Scheme 1: Synthesis of pyrazol-chromeno[2,3-d]pyrimidinones.

After optimizing the reaction conditions, the best conditions were applied for the synthesis of other derivatives using several salicylaldehydes **4a-d**, barbituric acid derivatives **5a-b**, and pyrazolones **3a-d**, as shown by the results in Scheme 1 and Table 3. By applying these conditions, the reactions were carried out easily to produce pyrazol-chromeno[2,3-*d*]pyrimidinone derivatives **6a-i** in good to excellent yields. The products were characterized by melting points, ^{1}H NMR, ^{13}C NMR, MS and FT-IR spectroscopic analyses. Melting points of the three known products were compared with the reported values in literature as shown in Table 3.

The proposed mechanism for preparation of pyrazol-chromeno[2, 3-*d*]pyrimidinones is shown in Scheme 2. Initially, the carbonyl group of salicylaldehyde derivative **4** is firstly protonated using SBA-Pr-SO_3H. Subsequently, the resulting SBA-Pr-SO_3^- converts barbituric acid **5** to its enolic form of **5'**. Then, the latter attacks to the activated carbonyl group of **4'** to produce intermediate **7**. Intermediate **9** is obtained through removal of a water molecule from **7**, an intramolecular cyclisation and again water removal, respectively. Through a Michael addition, pyrazolone **3** is added to the **9** and the final product **6** is achieved after tautomerization.

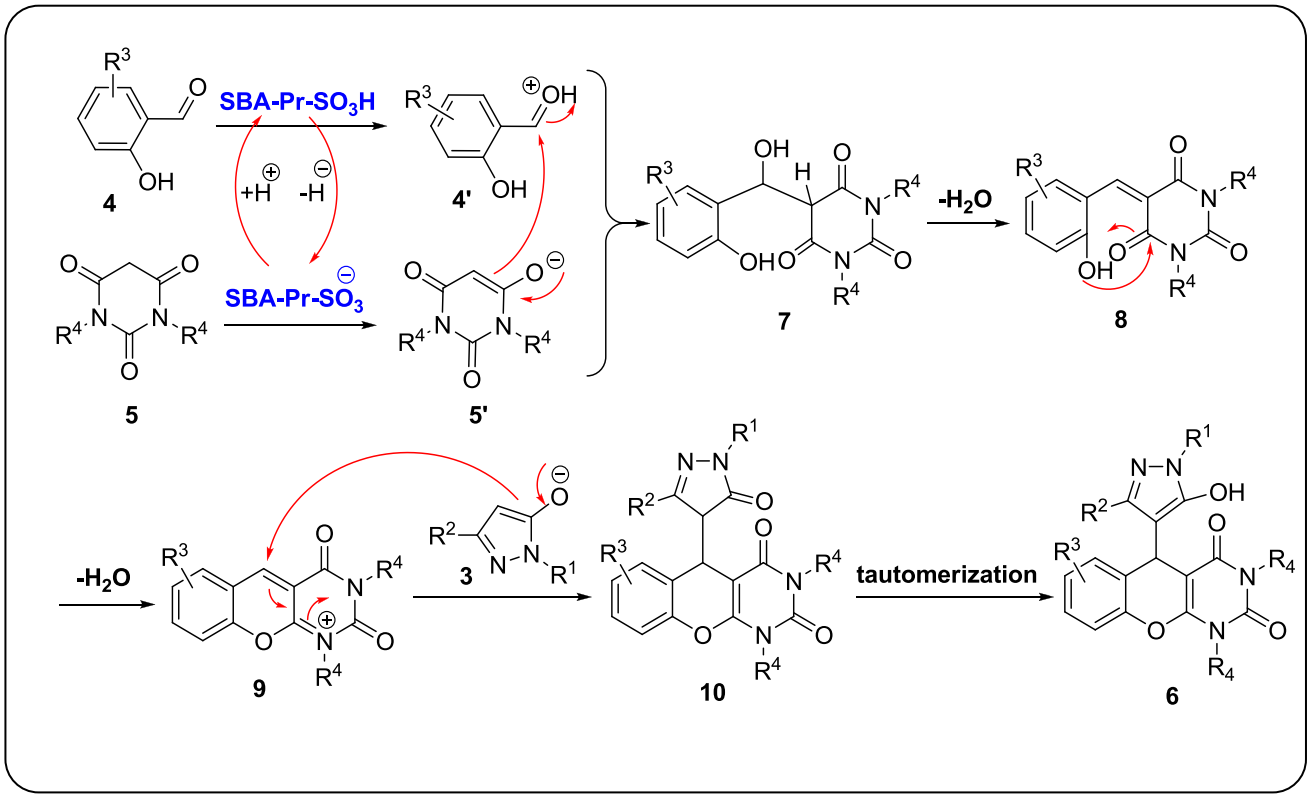
The only reported synthetic procedure for the preparation of pyrazol-chromeno[2, 3-*d*]pyrimidinones is shown in Table 4. Soleimani and coworkers synthesized compound **4a** within 12 h and using a homogeneous catalyst [33]. Therefore, the present methodology provides the better and greener conditions to gain

Table 3: Synthesis of pyrazol-chromeno[2,3-d]pyrimidinone derivatives.

Entry	No.	R^1	R^2	R^3	R^4	Time(h)	Yield (%)	m.p. (°C)	m.p. Lit. (°C)
1	6a	Ph	CH_3	H	H	5	90	296-298	284-287 [33]
2	6b	Ph	CH_3	5-Br	H	6	85	289-290	280-282 [33]
3	6c	Ph	CH_3	3-OMe	H	6	85	263-265	270-272 [33]
4	6d	4-NO_2Ph	CH_3	H	H	5	98	230-232	new
5	6e	CH_3	H	H	H	5	97	250-252	new
6	6f	CH_3	H	H	CH_3	3	85	234-236	new
7	6g	CH_3	H	5-NO_2	H	6	80	243-245	new
8	6h	CH_3	H	5-NO_2	CH_3	5	95	237-239	new
9	6i	Ph	H	5-NO_2	CH_3	5	90	218-220	new

Table 4: Comparing different conditions used for the synthesis of 4a.

Entry	Catalyst	Solvent	Conditions	Yield (%)	Time (h)	Year
1	*p*-TSA	H_2O/EtOH mixture	70 °C	95	12	2015 [33]
2	SBA-Pr-SO_3H	H_2O	Reflux	90	5	This work



Scheme 2: The proposed mechanism for the synthesis of pyrazol-chromeno[2, 3-d]pyrimidinones.

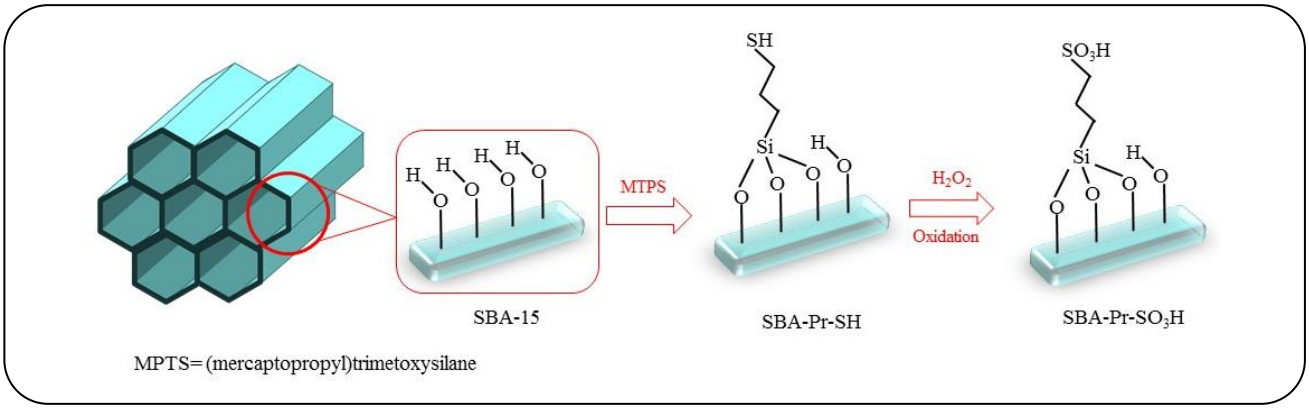


Fig. 1: Preparation of SBA-Pr-SO3H.

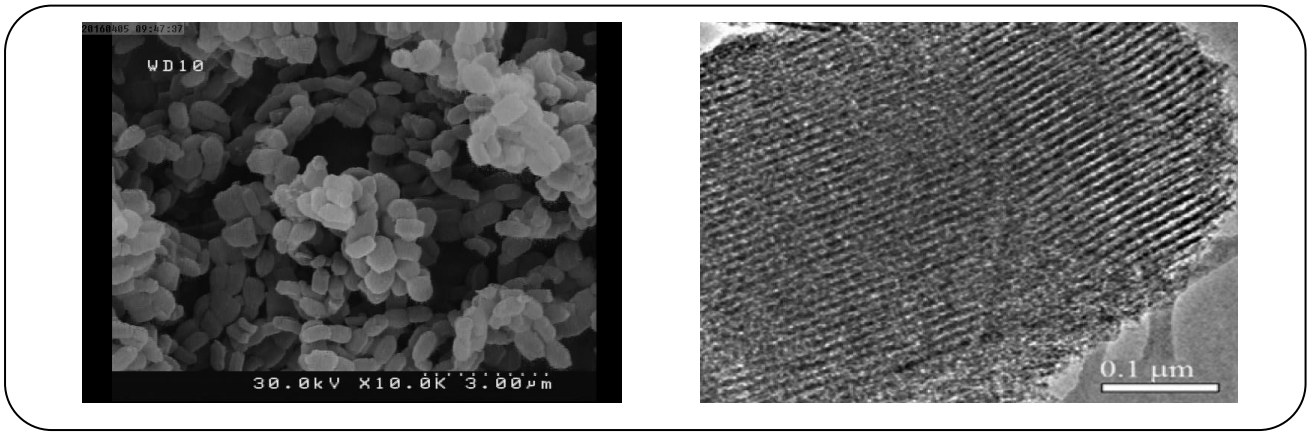


Fig. 2: The SEM (left) and TEM (right) images of SBA-Pr-SO3H.

pyrazol-chromeno[2, 3-*d*]pyrimidinones within lower reaction time using a heterogeneous solid acid catalyst.

Preparation of SBA-Pr-SO3H

The SBA-15 was synthesized through the method which was published before by *Zhao et at*. [34] The internal surface of prepared SBA-15 was then functionalized with (3-mercaptopropyl)trimethoxysilane (MPTS) followed by oxidation of thiol groups to sulfonic acid using hydrogen peroxide (Fig. 1). Analyzing the catalyst surface was accomplished by different techniques such as ThermoGravimetric Analysis (TGA), Brunauer–Emmett–Teller (BET) analysis, and elemental analysis (CHN) which proved that the propylsulfonic acid groups were immobilized well into the pores. The average pore diameter, surface area and pore volume of SBA-Pr-SO_3H, calculated by BET and BJH, were 440 m^2 g^{-1}, 6.0 nm, and 0.660 cm^3/g, respectively, which are smaller than those of SBA-15 due to the immobilization of sulfonosilane groups onto the pores [35]. The TGA analysis of SBA-Pr-SO_3H displayed a weight reduction in the temperature the range between 200-600 °C corresponded to the amount of organic group (1.2 mmol/g). The SEM image of SBA-Pr-SO_3H (Fig. 2-left) indicated uniform particles about 1µm; the identical morphology was observed for SBA-15. It can be concluded that the morphology of acid catalyst was saved without any changes during the process of surface modification. Besides this, the TEM image (Fig. 2-right) distinguish the parallel channels, which are similar to the pores configuration of SBA-15. This shows that the pore of SBA-Pr-SO_3H was not collapsed during two steps reactions.

Antimicrobial and antifungal tests

All products were investigated for the antimicrobial test against some Gram-positive bacteria including *Bacillus subtilis* (ATCC 465) and *Staphylococcus aureus* (ATCC 25923), Gram-negative bacteria including *Pseudomonas aeruginosa*

Table 5: Inhibition zone (mm) of synthesized compounds against bacteria and fungus obtained from disc diffusion method.

Compound	*B. subtilis*	*S. aureus*	*E. coli*	*P. aeruginosa*	*C. albicans*
6a	0	0	0	0	0
6b	0	0	0	0	0
6c	11	11	0	0	0
6d	14	0	0	0	0
6e	0	0	0	0	0
6f	0	13	0	0	0
6g	10	0	0	0	0
6h	10	0	0	0	0
6i	14	0	0	0	0
Chloramphenicol	26	22	24	8	-
Gentamicin	28	20	20	18	-
Nystatin	-	-	-	-	18

Table 6: Minimum inhibitory concentration (µg/ml) of synthesized compounds against bacteria and fungus.

Compound	*B. subtilis*	*S. aureus*	*E. coli*	*P. aeruginosa*	*C. albicans*
6a	>1024	>1024	>1024	>1024	>1024
6b	>1024	>1024	>1024	>1024	>1024
6c	512	512	>1024	>1024	>1024
6d	>1024	>1024	>1024	>1024	>1024
6e	>1024	>1024	>1024	>1024	>1024
6f	>1024	256	>1024	>1024	>1024
6g	1024	>1024	>1024	>1024	>1024
6h	1024	>1024	>1024	>1024	>1024
6i	>1024	>1024	>1024	>1024	>1024
Chloramphenicol	4	8	4	256	-
Gentamicin	0.125	0.5	0.5	1	-
Nystatin	-	-	-	-	8

(ATCC 85327) and *Escherichia coli* (ATCC 25922) and for antifungal activity against *Candida albicans* (ATCC 10231) *via* the disc diffusion method. Their Minimum Inhibitory Concentration (MIC) was also determined by microdilution method and compared with the commercial Chloramphenicol, Gentamicine, and Nystatin. Generally, the compound having a low MIC (below 10) and high IZ (above 20) can be considered as an antibacterial agent. For example, the MIC and IZ for Gentamicin against *B. subtilis* are 28 and 0.125, respectively, which shows it can effectively act against this bacteria. As shown in Table 5, IZ of products against the bacteria and fungus are not as well as those of the commercial antibiotics. Also, the MIC results of products (Table 6) are above 512, which is not favorable and therefore all compounds showed no significant antibacterial and antifungal activities.

CONCLUSIONS

This method described a green, clean and simple procedure for the synthesis of pyrazol-chromeno[2,3-*d*]pyrimidinones through the reaction of salicylaldehydes, barbituric acid, and pyrazolone in the presence of SBA-Pr-SO_3H as a nano and green solid acid catalyst.

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